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ABSTRACT (Maximum 200 words)

This report results from a contract tasking University of BARI as follows: The kinetics of nozzle expansion flow is a topic of large interest due to its linking with technological applications. Usually one can treat the problem by using two approaches. The first one is to use complicated 2D fluid dynamics codes with poor kinetics, the second one is to use 1D nozzle codes emphasizing the role of chemical kinetics in affecting the whole fluid-chemical problem. The second approach has been used by our group to characterize simple gases such as H2, N2, O2 and their mixtures. The peculiarity of our approach is to describe each vibrational level of the molecule as a new species thus avoiding the concept of vibrational temperature. This approach could be in principle extended to polyatomic molecules even though in this case the state tot state kinetics becomes a very difficult problem. These concepts will be developed in the present proposal which deals with the characterization of the kinetics of NH3 through nozzles of different geometries. Our proposal consists of different steps including: 1) development of a realistic kinetics for ammonia decomposition, 2) development of a realistic macroscopic model for vibrational deactivation of polyatomic molecules, 3) evaluation of the dependence of rates on vibrational temperature, 4) insertion of points 1-3 in the nozzle equations and 5) examination of results for different nozzle geometries.

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A MODEL FOR AMMONIA SOLAR THERMAL THRUSTER
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Introduction

Recently, solar thermal propulsion (STP) engines have been investigated as a promising technology to improve the capabilities of small satellites. In the Surrey Space Centre [1,2], a microscale engine has been designed to use ammonia as propellent. The main advantages of ammonia propellent are its sufficiently low molar mass and its chemical inertia at room conditions (not as dangerous as hydrazine).

To get better performances the ammonia gas, in the heat exchanger, should be dissociated in N_2 and H_2 species, doubling the particle density. Unfortunately the dissociation kinetics, at temperatures of interest in the engine, is so slow that the complete thermal dissociation of ammonia molecules could not occur.

In this project we have developed a kinetic model for an ammonia mixture flowing into the nozzle investigated in previous studies [1,2]. It is worth noting that we have introduced a state-to-state kinetics to verify the presence of non-equilibrium vibrational distributions during the nozzle expansion.

Nozzle Geometry

The nozzle used in the thruster has a conic geometry of the following dimensions (in mm):

throat radius	0.35
exit radius	2.0
exit-throat distance	6.2
inlet radius	1.0
inlet-throat distance	1.2

These data have been provided by the Surrey Laboratories. The converging nozzle is quite short so we choose to include part of the reservoir in the calculation through a connecting cone of the following dimensions (in mm)

reservoir radius	11.25
connecting cone length	2.0

The nozzle is presented on fig 1.

The fluid dynamic model of the nozzle flow is based on the almost one-dimensional Euler equations for a variable section duct. The Euler equations are solved, at the stationary state, together with the perfect gas equation of state and the mass continuity for each species including the reaction contributions. The numerical scheme adopted is described in [3].

Chemical Model

To build the chemical kinetic models, we need to select both the species that must be taken into account and their mutual reactions. In the laboratory experiments, the

pressure ranges from 1 to 4 atm and the temperature is less than 1500 K. The pressure values are measured directly, but the gas temperature is estimated only from some measurements performed outside the reservoir. This results in a large incertitude on the actual conditions operating inside the reservoir. In these context the ammonia decomposition kinetics is quite slow. Surface dissociation, neglected in this preliminary approach should, probably, be inserted in the model.
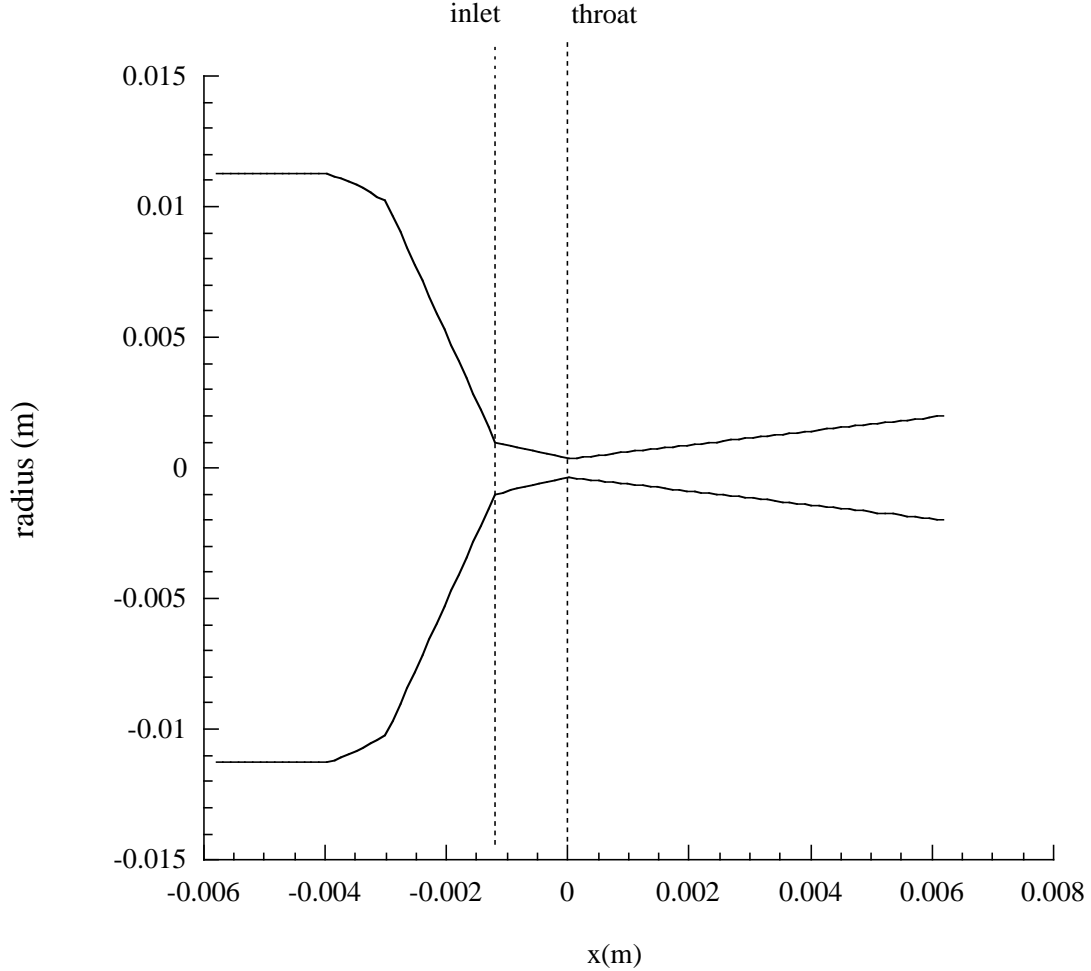

Fig. 1: Nozzle profile.

1. Species

We assume that the ammonia mixture consists of atoms and molecules formed in the NH_3 decomposition. We ignore all the ions because the temperatures involved are quite low. We introduce the vibrational excitation only for N_2 and H_2 molecules, which have stable vibrational excited levels. For all the other molecules, we diregard the internal levels as their number is so high that the computational load becomes unaffordable. Multitemperature model could be a valid approach assuring an acceptable computational effort nevertheless, in this work, we consider these internal states in equilibrium with the translational degree of freedom or as following a frozen kinetics. According to the internal state model selected we assign the C_p and γ ($\gamma = C_p/C_v$) coefficients to each molecule. For each vibrational mode or rotational axis, in equilibrium with the translational degree of freedom, we add the quantity αR into the expressions of C_p and C_v, where R represents the universal gas constant and the α parameter is set to 1 for a vibrational mode and to ½ for a rotational axis. This

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approximation is valid for the rigid rotor and for the infinite harmonic oscillator, since in general the C_p coefficient depends on the temperature. For atomic species no internal degree of freedom is considered. The contribution of translational degrees to the molar specific heat is 1.5R. Table 1 reports the species accounted and their relative properties.

Tab. 1: species inserted and their physical properties. Rot is the number of independent rotational axis, Vib the number of vibrational modes and E_f the enegy of formation.

Species	Mass (AMU)	Rot	Vib	E_f (eV)
NH_3	17	3	6	-0.403242
N_2H_3	31	3	9	4.30994
NH_2	16	3	3	2.00285
NH	15	2	1	3.90225
N_2	28	2	1	0.00000
H_2	2	2	1	0.00000
N	14	0	0	4.87950
H	1	0	0	2.23910

For H_2 and N_2 we estimate the energy of each vibrational level (ε_v) through the semi-empirical formula, function of the vibrational quantum number and of some spectroscopic constants expressed in cm^{-1}:

$$\varepsilon_v = \frac{hc}{e}\left[\omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + \omega_e y_e\left(v+\frac{1}{2}\right)^3 + \omega_e z_e\left(v+\frac{1}{2}\right)^4\right]$$

The H_2 spectroscopic constants have been obtained through the fits of the vibrational level energies extracted from the BKMP potential energy surface [4] while for N_2 we used data from ref. 5. Table 2 summarizes those values for the two species.
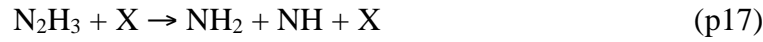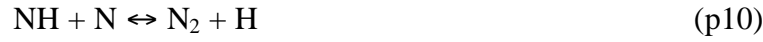
Tab. 2: Spectroscopic constants (in cm^{-1}) used in the calculation of the vibrational level energies.

Parameter	N_2	H_2
ω_e	2358.57	4464.7
$\omega_e x_e$	14.324	146.93
$\omega_e y_e$	-0.00226	4.7108
$\omega_e z_e$	0.0	-0.22712
E_{diss}	9.7639	4.4772
V_{max}	48	15

2. Processes

We implement in our model a macroscopic kinetics for NH_3 depletion introducing the following processes:

$NH_3 + X \leftrightarrow NH_2 + H + X$	(p1)
$NH_3 + X \leftrightarrow NH + H_2 + X$	(p2)
$NH_3 + H \leftrightarrow NH_2 + H_2$	(p3)

NH + H + X ↔ NH$_2$ + X	(p4)
H$_2$ + N + X ↔ NH$_2$ + X	(p5)
NH$_2$ + H ↔ NH + H$_2$	(p6)
NH$_2$ + NH$_2$ ↔ NH$_3$ + NH	(p7)
N + H + X ↔ NH + X	(p8)

NH + H ↔ H$_2$ + N	(p9)
NH + N ↔ N$_2$ + H	(p10)
NH + NH ↔ H$_2$ + N$_2$	(p11)
2H + N$_2$ ↔ H$_2$ + N$_2$	(p12)
2H + H$_2$ ↔ H$_2$ + H$_2$	(p13)
2N + N$_2$ ↔ N$_2$ + N$_2$	(p14)
2N + N ↔ N$_2$ + N	(p15)
NH$_3$ + NH$_2$ → N$_2$H$_3$ + H$_2$	(p16)
N$_2$H$_3$ + X → NH$_2$ + NH + X	(p17)
N$_2$H$_3$ + H → 2NH$_2$	(p18)
N$_2$H$_3$ + H → NH$_3$ + NH	(p19)

where X is a generic component. The rate coefficients for all these processes are expressed in the Arrhenius form:

$$K = K_0 T^\alpha e^{-E_a/T}$$

For the direct reaction, the parameters K_0, α and E_a are reported in table 3. The rate coefficients of these processes have been taken from ref. [5-10]. In this model, we neglect more complex molecules, such as N_2H_4, that do not seem to be significant.
Rates for the reverse processes have been obtained through the detailed balance principle

$$K_r = \frac{K_d}{K_{eq}}$$

where K_{eq} is the equilibrium constant. Equilibrium constants have been calculated, from partition functions, following the classical statistical thermodynamic theory [11] subsequently they have been fitted by the general equation

$$\ln(K_{eq}) = K_\infty + K_p \left(\frac{1000}{T}\right)^{q_p} + K_e e^{-\frac{T}{q_e}}$$

We consider only the equilibrium constants for the generation of a new species from standard ones like N_2 and H_2 in nitrogen-hydrogen compounds formation. Therefore all the formation reactions can be synthesized as
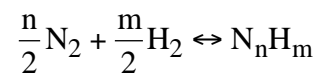
$$\frac{n}{2}N_2 + \frac{m}{2}H_2 ↔ N_nH_m$$

Table 4 presents the parameter values utilized to calculate K_{eq}, for the species listed in table 1.

Tab. 3: Arrhenius coefficients for the reactions inserted in the model. K_0 has the dimension of $cm^{3(n-1)}/s$, where n is the number of particles involved in the reaction, E_a is expressed in K and α is a dimensionless parameter.

process	K_0	α	E_a	Ref.
p1	1.53e-8	0	42400	[6]
p2	1.00e-9	0	47000	[4]
p3	3.20e-13	0.67	1720	[5]
p4	1.00e-32	0	0	[7]
p5	1.00e-34	0	0	[7]
p6	2.30e-13	0.67	2160	[5]
p7	6.64e-12	0	2800	[6]
p8	1.00e-33	0	0	[7]
p9	1.70e-12	0.68	957	[5]
p10	1.77e-11	0	0	[5]
p11	6.60e-13	0.55	957	[5]
p12	1.34e-31	-0.60	0	[5]
p13	2.68e-31	-0.60	0	[5]
p14	7.44e-32	-0.50	0	[5]
p15	3.31e-27	-1.50	0	[5]
p16	1.33e-12	0.5	10850	[4]
p17	1.70e-8	0.	21000	[4]
p18	2.60e-12	0	0	[4]
p19	1.70e-13	0	0	[4]

Tab 4: Coefficients used to calculate the formation equilibrium constants when the pressures are expressed in Pa.

Species	K_∞	K_p	q_p	K_e	q_e
NH_3	51.8293	-13.1631	0.960208	-7.97367	628.095
NH_2	19.6666	63.4542	1.01863	13.5452	311.287
NH	-5.14978	85.2911	0.998065	-2.21874	423.673
N	28.3772	-114.298	0.997620	-2.14877	4371.66
H	26.1506	-52.7759	0.996362	-2.71911	2157.34

From these formation equilibrium constants we can calculate the equilibrium constants relative to all the reactions involving the species in the table.

The kinetic model has been improved including a state-to-state kinetics for the diatomic species N_2 an H_2, substituting processes (P12-P15) with the state-selective dissociation and adding vibrational relaxation processes [12-14]. All the other processes involve only the ground state of such molecules.

Results

The kinetics of ammonia is not well known, even if this subject has been widely studied. The main problem is the kinetics slowness that prevents from estimating the kinetic constant precisely. Experimental works [1,2] on ammonia thrusters assume a complete decomposition of ammonia in the reservoir, but the kinetic scheme proposed does not permit to reach the equilibrium condition in an acceptable time for T<2000

K, even if the asymptotic value agrees to the equilibrium composition. For this reason we compare the results obtained starting from pure ammonia and from equilibrium concentrations.
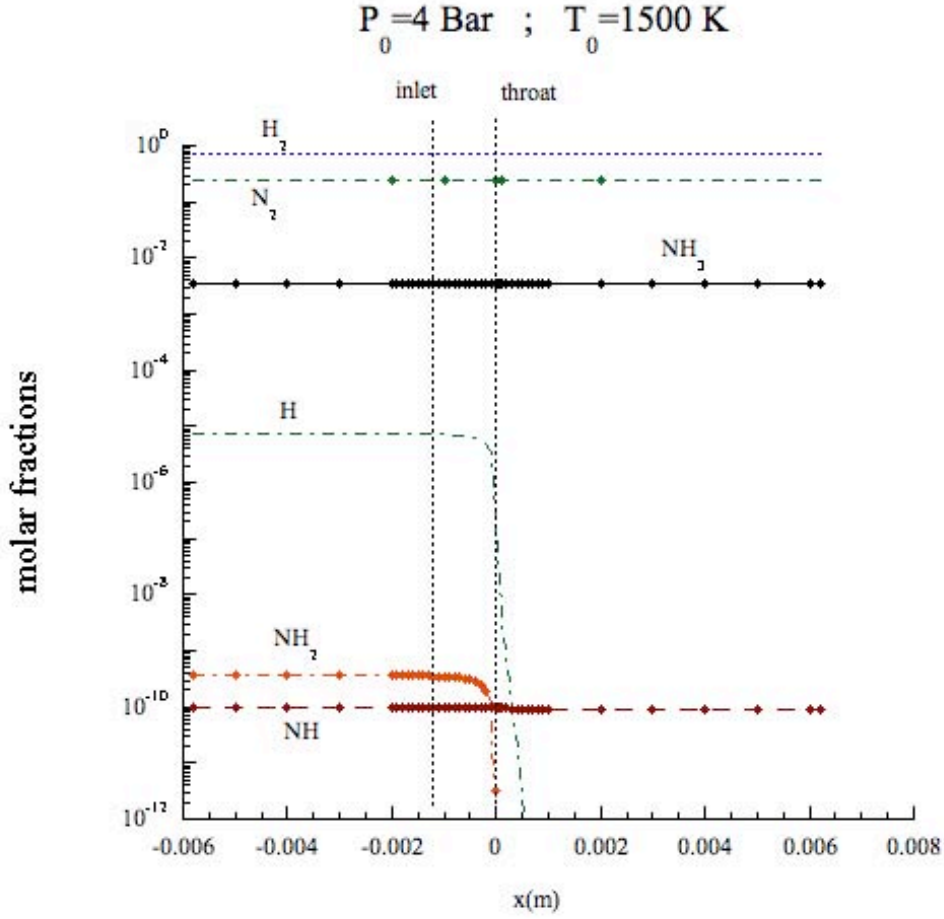

Fig. 2: Molar fractions of mixture species along the nozzle. We assume as reservoir conditions P_0=4 Bar and T_0=1500 K and start from an equilibrium inlet composition.

We investigate four different pressure values in the range 1-4 Bar. In figure 2 we report the concentration profile along the nozzle obtained for reservoir conditions of P=4 Bar and T=1500 K, and introducing the vibrational kinetics of N_2 and H_2.

Tab. 5: Mass flow rate and thrust of the nozzle as a function of the inlet pressure. The inlet temperature is T_0=1500 K except when marked with the "*" symbol assigned to T_0=2500 K. At inlet we suppose an equilibrium composition.

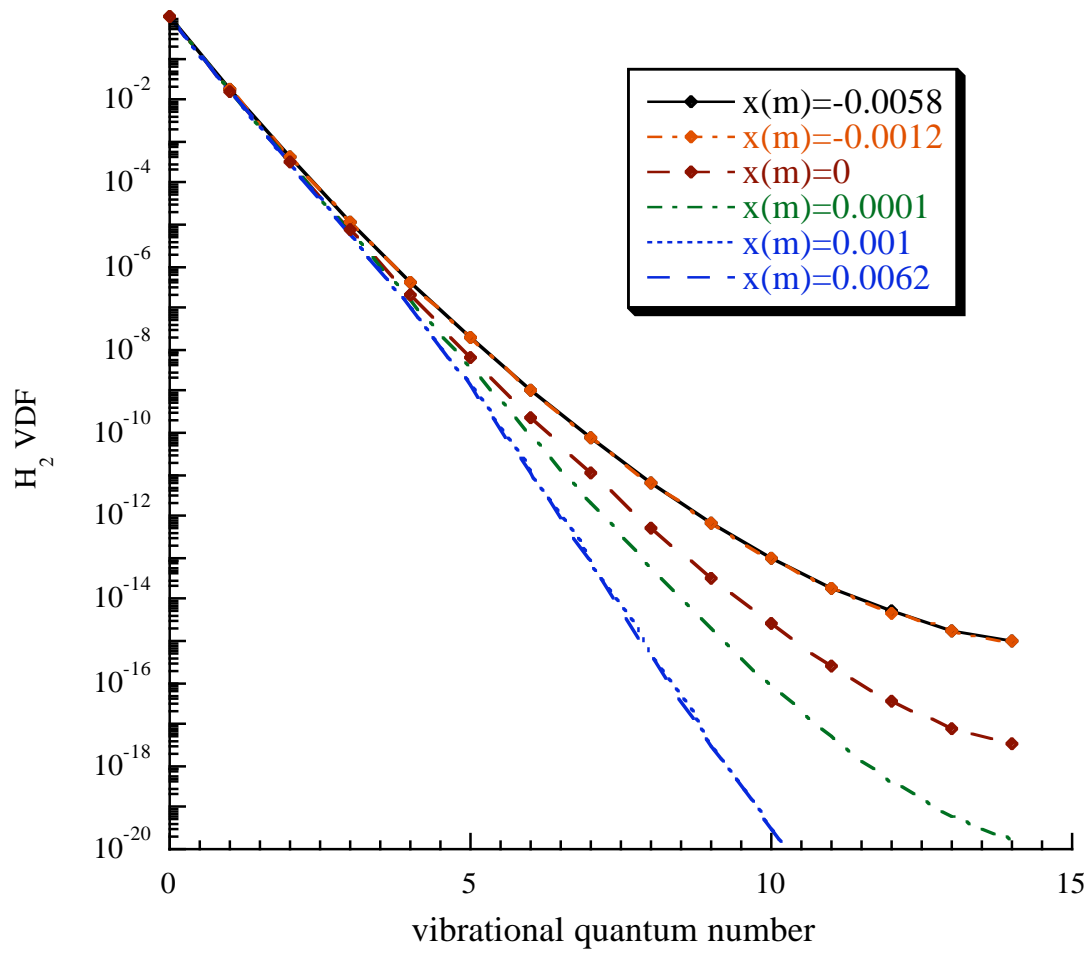| P_0(Bar)	mass flow rate (g/s)	thrust (mN)
1	2.1708e-2	64.337
2	4.3404e-2	128.68
3	6.5077e-2	192.97
4	8.6784e-2	257.38
4*	6.5954e-2	256.74

* T=2500 K

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Fig. 3: Hydrogen vibrational distributions at different nozzle positions in the same conditions as in fig. 2.

Tab. 6: Mass flow rate and thrust of the nozzle determined experimentally in different test cases.

mass flow rate (g/s)	thrust (mN)
.140	219
.147	223
.117	183
.121	190

Tab 7: Mass flow rate and thrust as a function of the inlet dissociation degree (α) of the ammonia. Inlet pressure and temperature are P_0=4 Bar and T_0=1500 K.

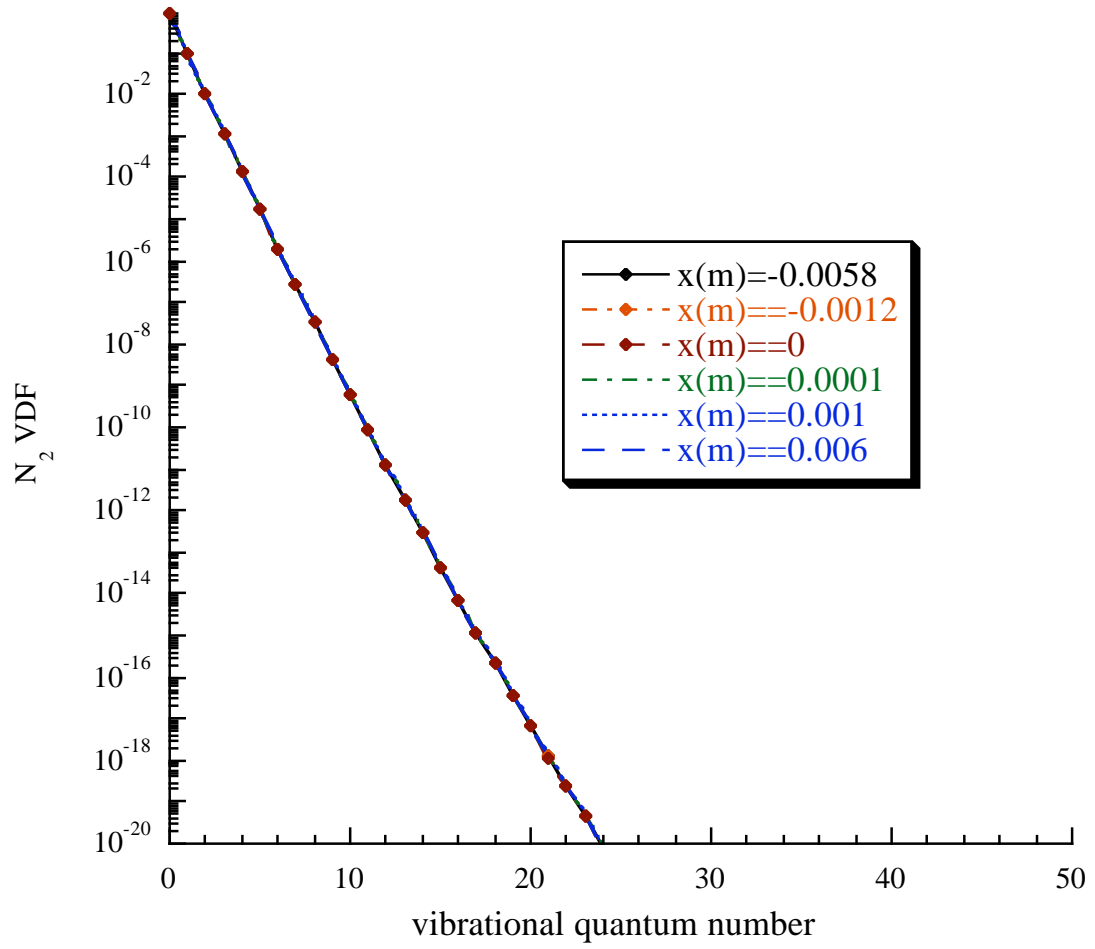| α	mass flow rate (g/s)	thrust (mN)
0.0	1.1189e-1	284.13
0.2	1.0437e-1	280.35
0.4	9.7946e-2	275.67
0.8	8.9483e-2	264.37
1.0	8.5450e-2	253.33

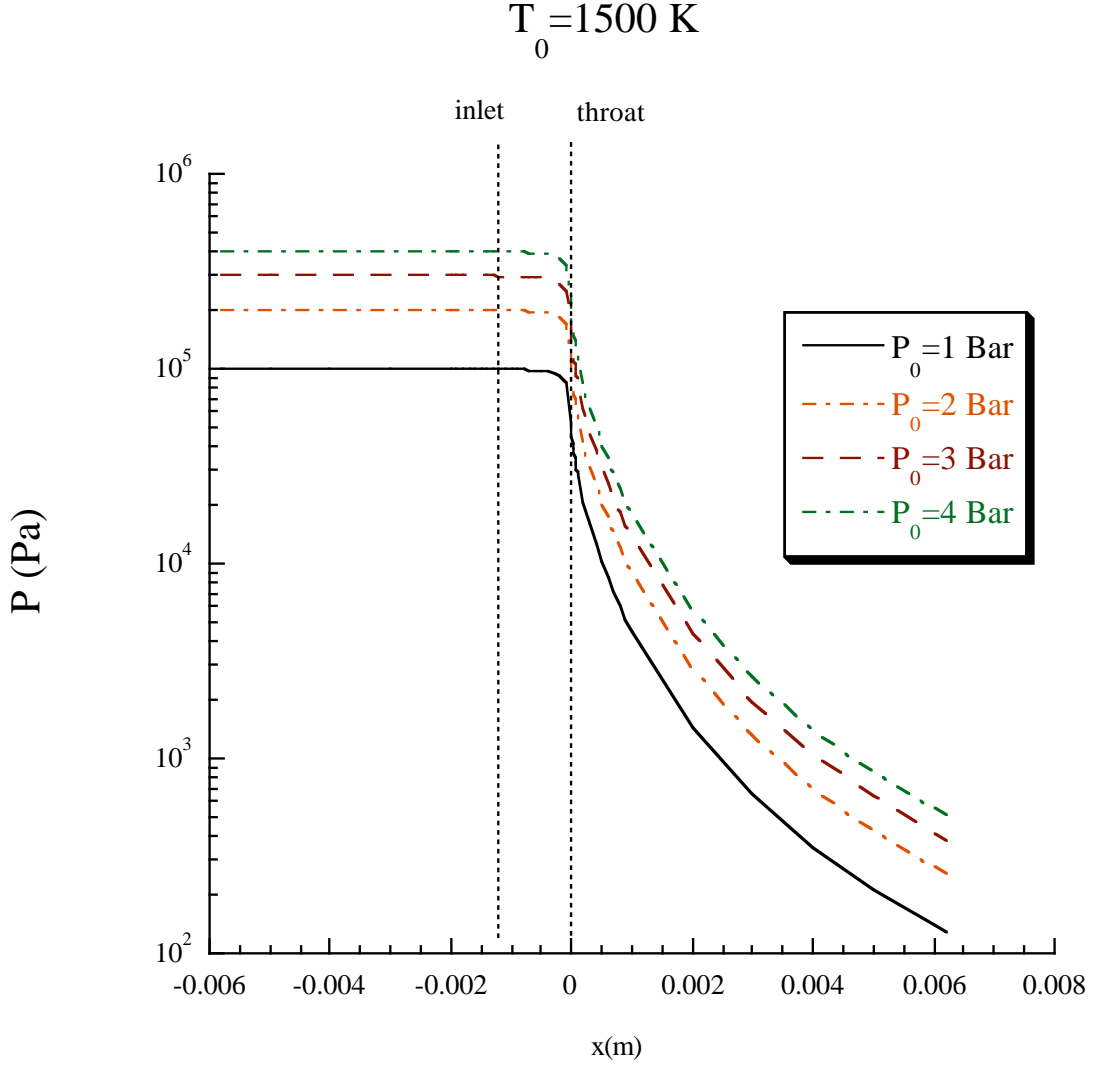Fig. 4: Nitrogen vibrational distributions at different nozzle positions in the same conditions as in fig. 2.

Fig. 5: Pressure profile along the nozzle as a function of the inlet pressure for T_0=1500 K and starting from an inlet equilibrium composition.

It is interesting to observe that the flow is practically frozen along the whole nozzle except for some minor species such as H and NH_2 that completely disappear at the nozzle exit. The atomic nitrogen molar fraction is lower than 10^{-10}.

Figures 3 and 4 describe the vibrational distribution of hydrogen and nitrogen for the conditions of figure 2. We can observe that the nitrogen distributions are frozen. On the contrary, while H_2 distributions, for $v\leq3$, are almost frozen, their tails are strongly depleted, resulting in non-Boltzmann distributions. The different behaviour of the two species is due to the different percentage of nitrogen and hydrogen atoms; hydrogen atom concentration is high enough so that the VT collisions involving atoms are fast enough to cool the distribution tails. We must point out that we neglect the vibrational depletion of $N_2(v)$ by atomic and molecular hydrogen collisions. We observe that the Mach number is practically independent on the initial temperature and pressure, obtaining at the nozzle exit a value close to Mach 5.4. We report the pressure along the nozzle in figure 5. It is quite interesting to note that the exit pressure is proportional to the inlet pressure. These two results occur as the chemistry weakly affects the macroscopic quantities during the expansion.

Table 5 displays the mass flow rate and the thrust for different inlet pressures at T_0=1500 K or T_0=2500 K. The agreement with the experimental results reported in table 6 is satisfactory, as the nozzle reservoir conditions (mainly the temperature) are not well known experimentally.

There are some incertitude in the chemistry model, because the dissociation of ammonia is very slow for T<2000 K. In such conditions the kinetic models published in the literature cannot provide the complete dissociation of ammonia in an acceptable time period. On account of this we also try as initial condition a pure ammonia gas.

Dissociation inside the reservoir and the nozzle is very poor, so that again in this case the flow is frozen. As a consequence, the flow properties depend only on the C_p/C_v ratio and on the mean molar mass, then the exit properties are completely different form the equilibrium case. As an example in figure 6 we compare the Mach numbers computed starting from an equilibrium composition (Eq.) and from pure ammonia (NoEq.). It is not possible to really know what composition prevails inside the reservoir for T<2000K, moreover some impurites or wall catalitic effects can accelerate the kinetics, bringing the system to equilibrium faster than predicted by our kinetic model.
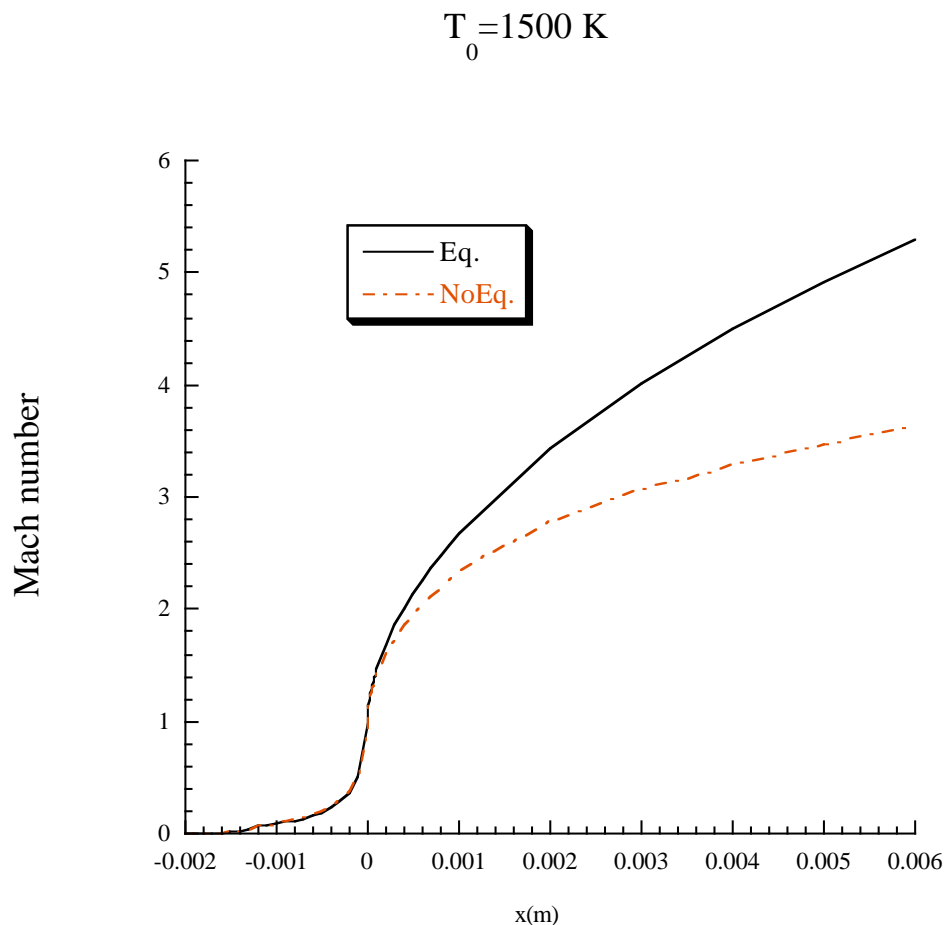
$$T_0 = 1500 \text{ K}$$

Fig. 6: Mach number profile compared for inlet equilibrium (Eq) and pure ammonia (noEq) case (pressure and temperature conditions as in fig 2).

We try the same comparison at T_0=2500 K. In this case, the mixture reaches the equilibrium composition in the reservoir. Nevertheless the Mach number profiles in

the equilibrium and non equilibrium case are again different (see fig. 7). This is the demonstration that the history of the gas in the reservoir is important.
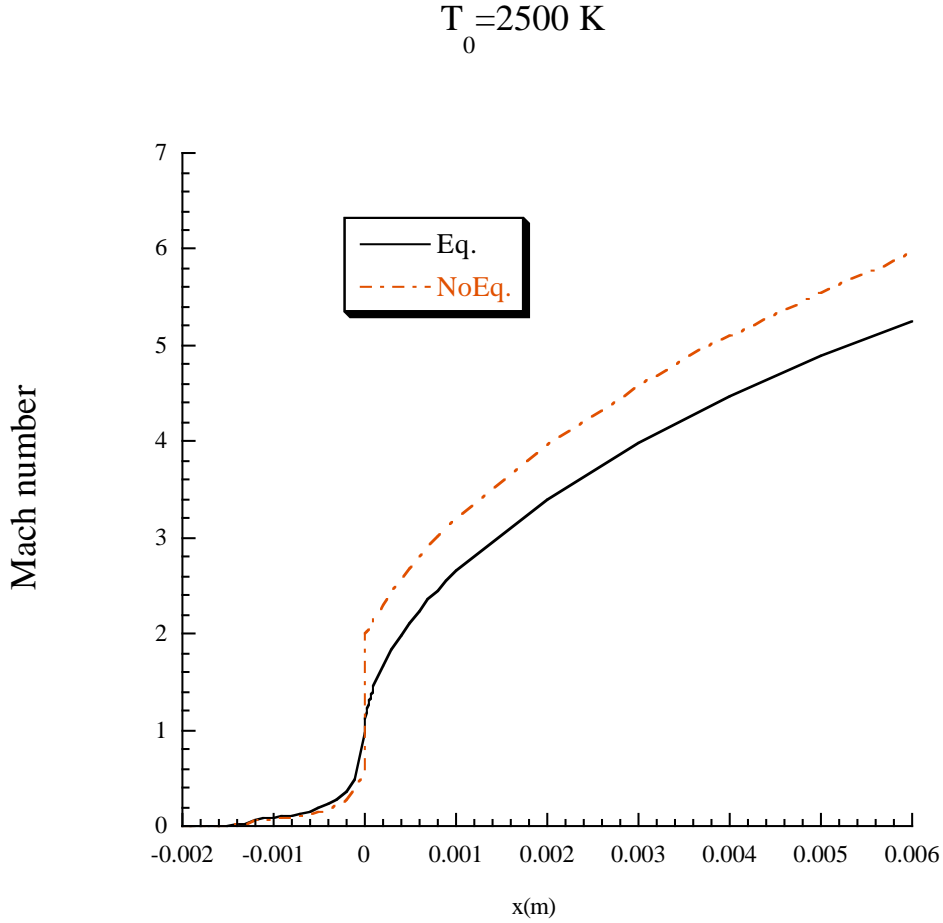
$$T_0 = 2500 \text{ K}$$

Fig. 7: Same as in fig 6 with reservoir temperature T_0=2500 K.

Effects of initial conditions propagate also on the temperature profiles. In figure 8 we show the normalized temperature profile calculated starting from an equilibrium condition (Eq.) and from an undissociated ammonia (NoEq.) for a reservoir temperature of 1500 K and a pressure of 4 Bar. We observe that the exit temperature is much higher in the case of the equilibrium condition. This behaviour could be due to the lower mean molar mass associated to the mixture in equilibrium composition inside the reservoir.

Different behaviours occur when the reservoir temperature reaches 2500 K (see fig. 9). In fact, at this temperature, the reactions in the inlet are faster than in the flow, therefore one can observe an increase of the temperature due to the mixture dissociation. Even if the ammonia energy is lower than that of nitrogen and hydrogen molecules, the compression due to the double particle number density produces an increase of the temperature. At the nozzle exit, the differences are lower than in the case of an inlet temperature of 1500 K.

We find similar behaviours for the relaxation of the vibrational temperature, calculated as the temperature of the first excited level (figure 10). Starting from non equilibrium conditions we can observe an increase of the vibrational temperatures following the gas temperature. At the nozzle exit the vibrational temperature freezes

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at a temperature higher than 2300 K just after the throat. N_2 vibrational temperature is practically frozen.

As a consequence of the previous results, we can state that there are some incertitudes about the inlet composition. At this purpose we have reported in table 7 the calculated mass flow rate and thrust for different dissociation degree "α" of ammonia for the process $NH_3 = 1.5\ H_2 + 0.5\ N_2$ defined as

$$\alpha = 1 - \frac{\left[NH_3\right]}{\left[NH_3\right] + .5\left[N_2\right]}$$

that ranges from 0 (pure ammonia) to 1 (N_2 and H_2 mixture). We note that both quantities decrease when the dissociation degree increases, but the thrust changes more slowly than the mass flow rate.
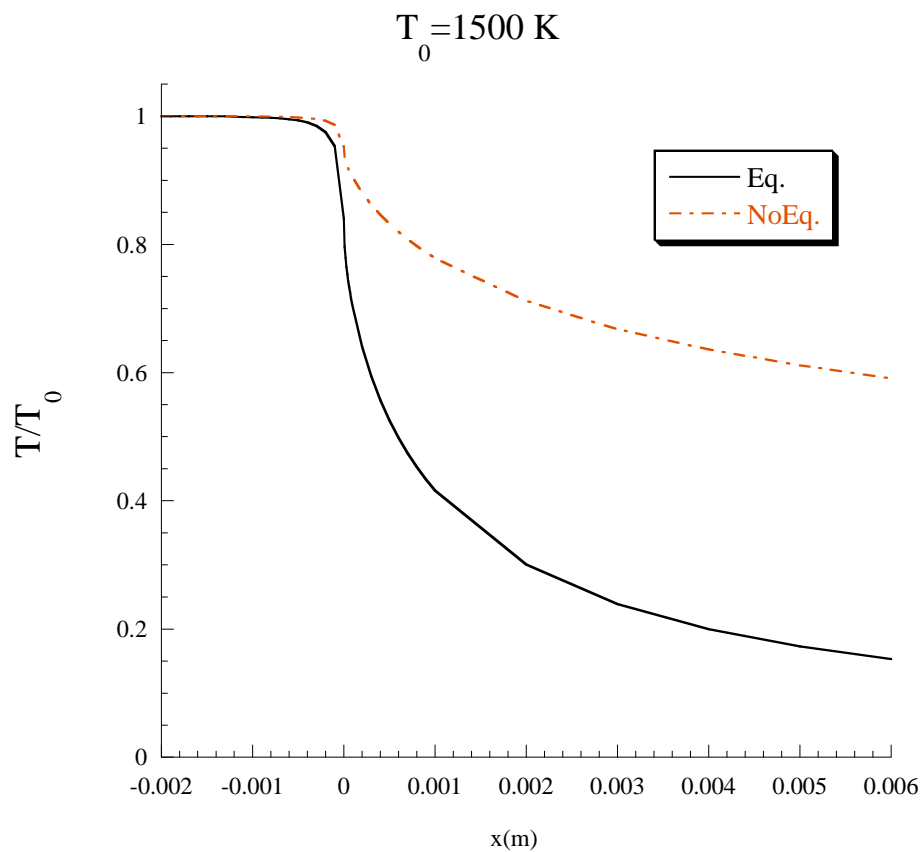

Fig. 8: Reduced temperature profile compared for inlet equilibrium (Eq) or pure ammonia (noEq) case, for a reservoir temperature $T_0 = 1500K$ (pressure and temperature conditions as in fig 2).

Conclusions.

In this study we investigate the role of chemical kinetics in modeling ammonia solar thermal engine. Many problems still need to be solved. In particular, the kinetic model has to be improved, insertion of some impurities or wall catalysis could speed up the dissociation kinetics.

A further improvement of the model could be the inclusion of non equilibrium in rotational and vibrational levels of species other than N_2 and H_2, even if it seems that, in the conditions the thruster runs, the vibrational kinetics is not so much effective.
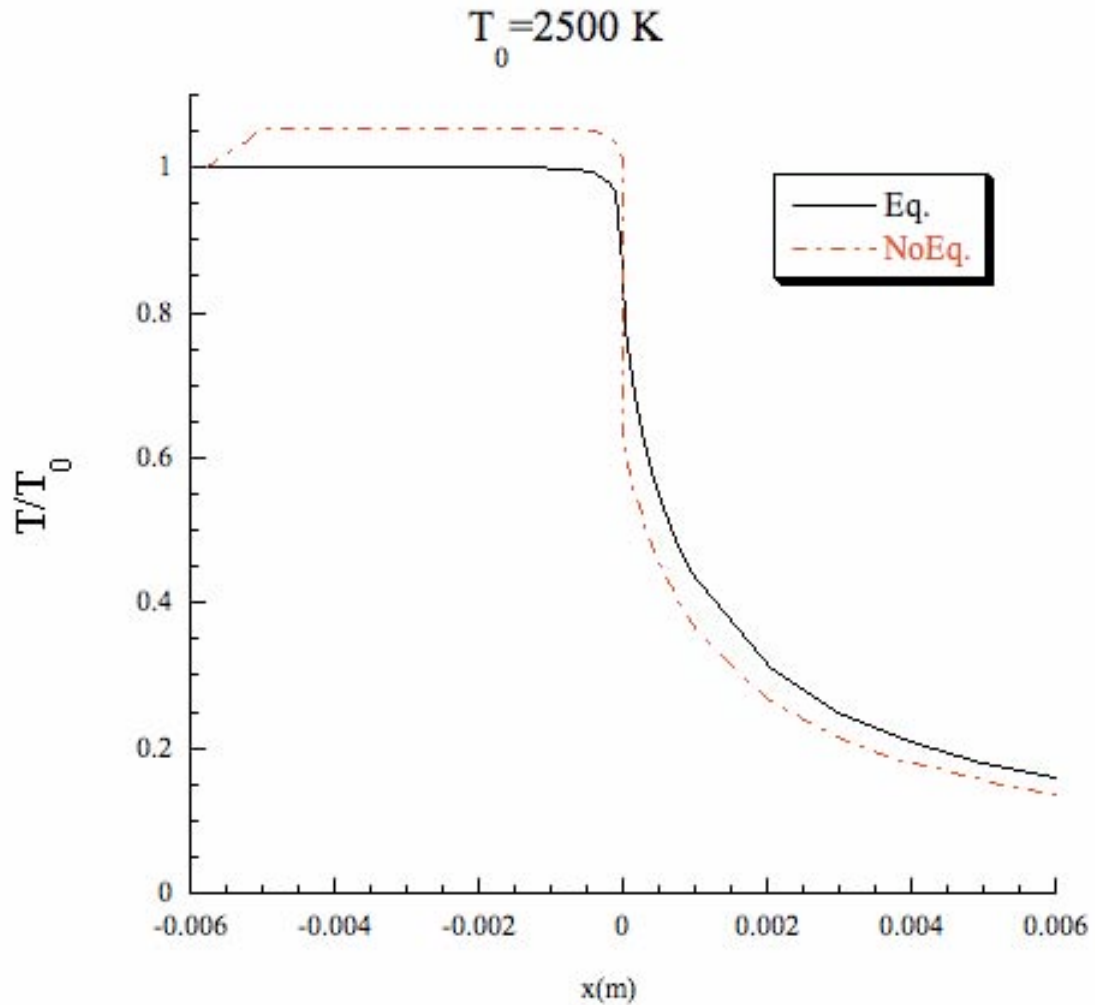

Fig. 9: Reduced temperature profile compared for inlet equilibrium (Eq) or pure ammonia (noEq) case, for a reservoir temperature $T_0 = 2500K$ (pressure and temperature conditions as in fig 2).
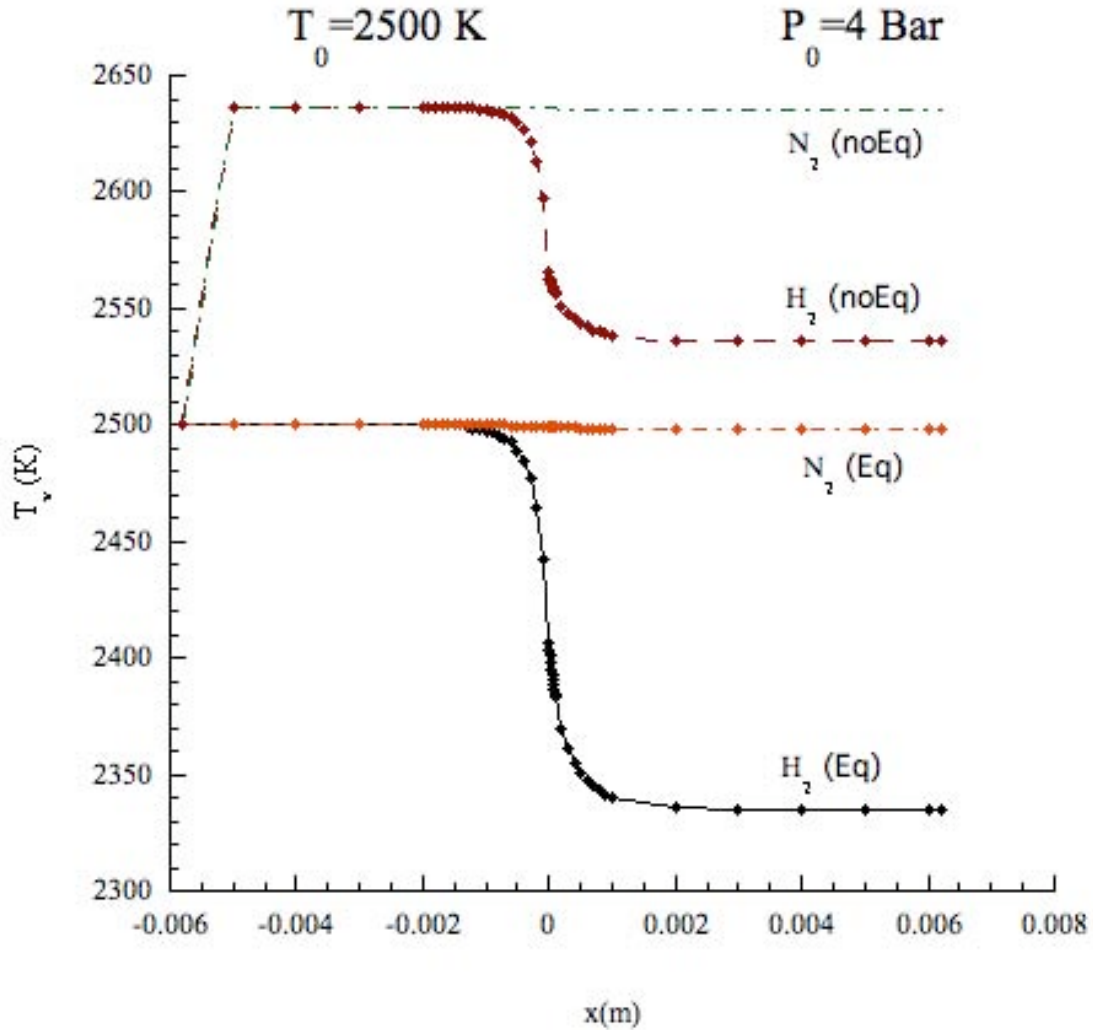
Fig. 10: Vibrational temperature (T_v) profile of N_2 and H_2 in the same conditions as in figure 9.

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